# Acid Base extraction - Separation of a Mixture

## Introduction and Background

The solubility of organic acids and bases in water can be changed greatly by changing the pH. Except for compounds containing fewer than six carbons, most carboxylic acids, phenols, and amines are insoluble or only slightly soluble in water. However, carboxylic acids and phenols dissolve in dilute aqueous sodium hydroxide solution (pH>>7) and amine dissolve in dilute aqueous hydrochloric acid solution (pH<<7) because carboxylic acids and phenols react with bases to form salts.

\[
\text{RCO}_2\text{H} (l/s) + \text{NaOH} (aq) \rightarrow \text{RCO}_2\text{Na} (aq) + \text{H}_2\text{O} (l)
\]

\[
\text{ArOH} (l/s) + \text{NaOH} (aq) \rightarrow \text{ArONa} (aq) + \text{H}_2\text{O} (l)
\]

Amines like ammonia react with acids to form salts

\[
\text{RNH}_2 (l/s) + \text{HCl} (aq) \rightarrow \text{RNH}_3\text{Cl} (aq)
\]

The salts are soluble in water because they are ionic.

A mixture containing a water insoluble organic acid, a water insoluble organic base, and a water insoluble neutral compound can be separated by dissolving the mixture in an organic solvent which is not soluble in water, and then extracting the solution first with dilute hydrochloric acid, and then with dilute sodium hydroxide solution as shown in the flow chart below.

The neutral compound can be recovered by evaporation (or, if necessary, fractional distillation of the solvent).

The amine can be recovered from the water solution of its salt by making the acidic solution basic.

\[
\text{RNH}_3\text{Cl} (aq) + \text{NaOH} (aq) \rightarrow \text{RNH}_2 (l/s) + \text{NaCl} (aq)
\]

If it is a solid, the amine is collected by filtration. If it is a liquid, it is taken up in the organic solvent (that is, its volume is increased by adding more solvent to reduce the mechanical loss), the solution is separated, and the solvent evaporated.
The acid can be recovered from the water solution of its salt by making the basic solution acidic by adding HCl solution.

\[
\text{RCO}_2\text{Na (aq) + HCl (aq) } \rightarrow \text{RCO}_2\text{H (l/s) + NaCl (aq)}
\]

The acid is collected by filtration or by taking it up in the solvent, separating, and evaporating. The extraction of a water insoluble organic acid from solution in an organic solvent by extraction with dilute aqueous sodium hydroxide solution can be understood in terms of the equilibrium between the acid and its various forms.

**Equilibrium (1):** \( \text{RCO}_2\text{H (org)} \rightleftharpoons \text{RCO}_2\text{H (aq)} \)

**Equilibrium (2):** \( \text{RCO}_2\text{H (aq)} \rightleftharpoons \text{RCO}_2^-\text{(aq)} + H_3O^+\text{(aq)} \)

Because hydroxide ions react with hydronium ions to form the weak electrolyte water

\[
\text{OH}^-\text{(aq) + H}_3\text{O}^+\text{(aq) } \rightarrow \text{2H}_2\text{O (l)}
\]

Equilibrium (2) is shifted to the right by the addition of hydroxide ions. Shifting Equilibrium (2) to the right uses up \( \text{RCO}_2\text{H} \) molecules. Using up \( \text{RCO}_2\text{H} \) molecules in the water layer shifts the equilibrium (1) to the right. The acid goes from the organic layer into the water layer.

The extraction of a water insoluble amine from solution in an organic solvent by extraction with dilute aqueous hydrochloric acid can be understood similarly in terms of the equilibrium between the amine in the water layer and the amine in the organic layer, and the equilibrium between the amine and its conjugate acid in the water layer.

\[
\text{RNH}_2\text{(org) } \rightleftharpoons \text{RNH}_2\text{(aq)}
\]

\[
\text{RNH}_2\text{(aq) + H}_2\text{O (l) } \rightarrow \text{RNH}_3^+\text{(aq) + OH}^-\text{(aq)}
\]

**Safety**

*Warning:* Amines can be absorbed through the skin. Although the amines used in the unknown have been chosen for their low toxicity based on existing information, try not to get any of the unknown on your skin or clothing. If you do, wash immediately with lots of soap and water. If you find a basic compound in your unknown, follow the direction for disposing of it carefully.

**Experimental Part A: Separation of Mixture**

1. Weigh about 0.5 g of your unknown
2. Transfer the sample to a 20 mL test tube
3. Dissolve it in 5.0 mL of dichloromethane (CH2Cl2)
4. Extract the dichloromethane solution with 2.5 mL of 5% hydrochloric acid by adding the hydrochloric acid to the sample in the test tube
5. Cork the test tube firmly and shake it for two minutes.
6. Let the test tube stand until the layers have separated and then open carefully.
7. Use a Pasteur pipet to separate the layers. The top layer is the aqueous layer
8. Place the aqueous layer in a test tube labeled ‘HCl extract’
9. Extract the dichloromethane layer with another 2.5 mL portion of 5% HCl and combine the second HCl extract with the original.
10. Mix the combined HCl extract and test it with litmus paper to be sure that they are acidic. If they are not, repeat step 9 until the blue litmus turns red
11. Add 2.5 mL of H2O to the dichloromethane solution (water wash) and add the water wash to the HCl extract and set the HCl extract aside for Part B.
12. Now extract the dichloromethane solution with 2.5 mL of 5% NaOH
13. Repeat steps 5-7 above
14. Place the aqueous layer in a test tube labeled “NaOH extract”
15. Extract the dichloromethane layer with another 2.5 mL portion of 5% NaOH and combine the second NaOH extract with the original.
16. Mix the combined NaOH extract and test it with litmus paper to be sure that they are basic (not acidic). If they are not basic, repeat step 15 until the red litmus turns blue
17. Wash the dichloromethane layer with 2.5 mL of water, add water to the NaOH extract and set the NaOH extract for part B.
18. Add ~0.10 g anhydrous sodium sulfate (Na2SO4) to the dichloromethane solution
19. If the Na2SO4 clumps together, separate the dichloromethane solution by decantation, (make sure none of the Na2SO4 gets into the decanted solution) wash the sodium sulfate twice with 1 mL dichloromethane, and combine the dichloromethane solutions.
20. The repeat steps 18 and 19 until the sodium sulfate do not clump together anymore
21. Place a small boiling stone in a dry test tube labeled “Neutral Fraction”
22. Get the weight of the test tube and boiling stone
23. Transfer the dichloromethane solution to it
24. Rinse the original test tube with small amount of dichloromethane and combine with the solution in the pre-weighed test tube

Experimental Part B: Recovery of Components of Mixture from Solution

1. **Basic Fraction from HCl Extraction**
   1.1. Cool the HCl Extract in an ice bath
   1.2. Get 5 mL of 10% NaOH solution in a test tube and add it drop wise to the cooled HCl extract while stirring, until the solution becomes basic
   1.3. Scratch the sides of the test tube with the stirring rod to facilitate precipitation
   1.4. Separate the liquid from the solid by suction filtration
   1.5. Wash the solid twice with cold water
   1.6. Place the filter paper on paper towel and let the product dry.
   1.7. Get the weight of the dried product
   1.8. Get the MP of the dried product

2. **Acidic Fraction from NaOH Extraction**
   2.1. Cool the NaOH Extract in an ice bath
   2.2. Get 5 mL of 10% HCl in a test tube and add it drop-wise to the cooled NaOH extract while stirring, until the solution becomes acidic
   2.3. Scratch the sides of the test tube with the stirring rod to facilitate precipitation
   2.4. Separate the liquid from the solid by suction filtration
   2.5. Wash the solid twice with cold water
   2.6. Place the filter paper on a paper towel and let the product dry.
   2.7. Get the weight of the dried product
   2.8. Get the MP of the dried product

3. **Neutral Fraction**
   3.1. Evaporate the dichloromethane by warming the test tube in a water bath at 50°C.
   3.2. Place the test tube in a filter flask and stopper the flask.
   3.3. Aspirate the product in the test tube to remove trace amount of dichloromethane.
   3.4. Weigh the test tube and find the weight of the product by difference.
   3.5. Get the MP of the dried product.

Find the identity of the samples in the mixture from their MP and the chart provided. Calculate the percentage recovery of each fraction. Make a flow chart of the separation of the mixtures and the recovery of the basic, neutral, and acidic fractions.
<table>
<thead>
<tr>
<th>Questions</th>
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<tbody>
<tr>
<td>1. Why must the organic solvent be separated by extraction be insoluble in water?</td>
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<td>2. What is the purpose of washing with water after extraction with a reaction solvent?</td>
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<td>3. What is the purpose of using a tared test tube?</td>
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<td>4. Why is the aspirator used to evaporate the dichloromethane?</td>
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<td>5. Why should you not touch the crystals with your fingers?</td>
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<td>6. Which fraction was least pure? On what evidence you base your conclusion?</td>
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